C.I.P.S.

MODELE MATHEMATIQUE DE LA POLLUTION EN MER DU NORD.

TECHNICAL REPORT

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A.A.S. determination of copper, zinc, lead and cadmium contents of seawater by concentration on a Chelex 100 resin. Automatisation of the method.

by

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INTRODUCTION.

The determination of heavy metals concentration in a natural environment such as seawater is pratically impossible by atomic absorption spectrophotometry despite the specificity and high sensitivity of the method.

The very low concentrations which have to be measured are impossible to detect by the flame whereas the use of the graphite furnace is very difficult due to the strong matrix interferences.

A preliminary step was thus necessary, to both eliminate the matrix and concentrate the trace elements of seawater.

Two methods were often used until now : complexation followed by solvent extraction with APDC-MIBK and chelating ion exchange with Chelex 100 or Dowex A1 resins.
Our laboratory uses the latter method.

1.- Experimental.

E. JACOBS (1) for copper and L. GOEYENS (2) for lead investigated the efficiency with which these two elements can be concentrated from seawater by means of a resin Chelex 100 (50 - 100 mesh Bio-Rad Laboratories). They obtained a 100 % efficiency for the retention of copper and lead followed by a 2 M nitric acid elution.

Method used : 250 ml of sample are adjusted to a pH value of 7,6 and allowed to pass through the column at a flow rate which does not exceed 5 ml/min. The column is then washed with 15 ml of NaOH pH 8. The elution is performed with 50 ml of 2M nitric acid (flow rate : ± 2 ml/min.). They thus obtained a concentration factor of five and determined Cu and Pb in the eluate by flameless atomic absorption spectroscopy with a graphite furnace.

Since then following procedures have been automated : passing the sample through the resin, elution and measuring. The unit concentrating all these functions can either continuously operate as a pollution control station or as an autoanalyser treating about 15 samples/hour.

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(1) E. JACOBS : Thesis - Brussel -september 1973.

(2) L. GOEYENS: Thesis - Brussel -september 1973.

2.- Apparatus.

The installation works as follows : sample, washwater and 2.8 M nitric acid are pulsed to the column by a peristaltic pump at a constant and wellknown flow rate (± 4 ml/min). Their feeding order being determined by an assembly of pneumatic valves which are themselves driven by a set of cams.

Each cam drives, by means of a contact, the opening or closing of a valve during a preset and constant period. The movement of all the cams is in turn actuated by a motor performing one rotation in 90 minutes. This period represents thus the complete treatment period of one sample, i. e. :

- sample flow : 50'
- rinsing the column : 10'
- elution and regeneration : 15'
- rinsing the column : 15'

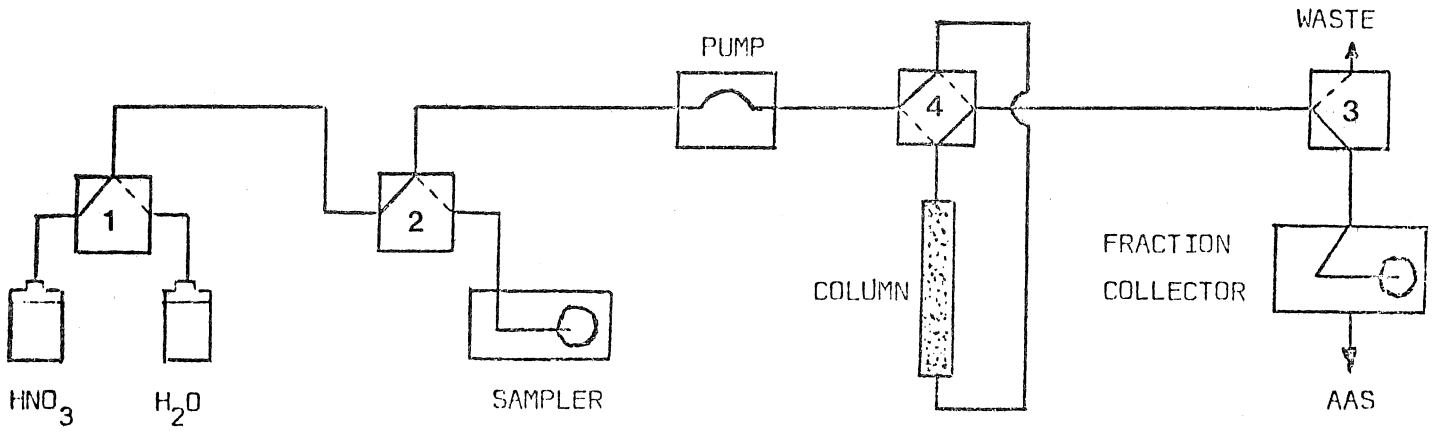
The samples are being distributed by means of an automatic sampler, itself being driven by 2 cams.

During the countercurrent elution, the eluate is recovered by a fraction- collector fitted with a drop counter.

The fractions (approx. 5 ml) are being collected in polyethylene tubes displayed on a drum.

This drum can in turn be fixed on an automatic sample distributor connected to an atomic absorption spectrophotometer.

The exact volume of the sample passed through the resin as well as the volume of the recovered fractions are determined by weighing.



1, 2, 3 : three-way valve

4 : four-way valve (allows regular or counter-current operation).

3.- Experimental results.

The recovery percentage after passing through the resin has been established not only for copper and lead but also for zinc and cadmium. Increments of those various metals spiked to deionised water and to 0.22 μm filtered seawater have been recovered with efficiencies varying between 95 and 105 %.

The manual method previously used in laboratory gave a concentration factor of approx. five ($\pm$ 250 ml of sample eluted by 50 ml nitric acid) and did thus not allow flame measurements but well graphite furnace ones, which is a method that is not easily automated. One thus had to increase this concentration factor, either by increasing the initial sample volume (which would have increased the passing time through the resin) or by decreasing the eluate volume.

The acid concentration and the pump throughput remaining constant for each sample, the heavy metals will normally be eluated within the same volume.
Analysing the various fractions recovered by the collector allows to locate this volume.

Graphs 1-2-3-4 show an example of elution curves achieved with zinc, copper, cadmium and lead.
As a rule, zinc and copper are completely eluted in a 5 ml volume, whilst cadmium and lead are generally spread over 2 fractions.

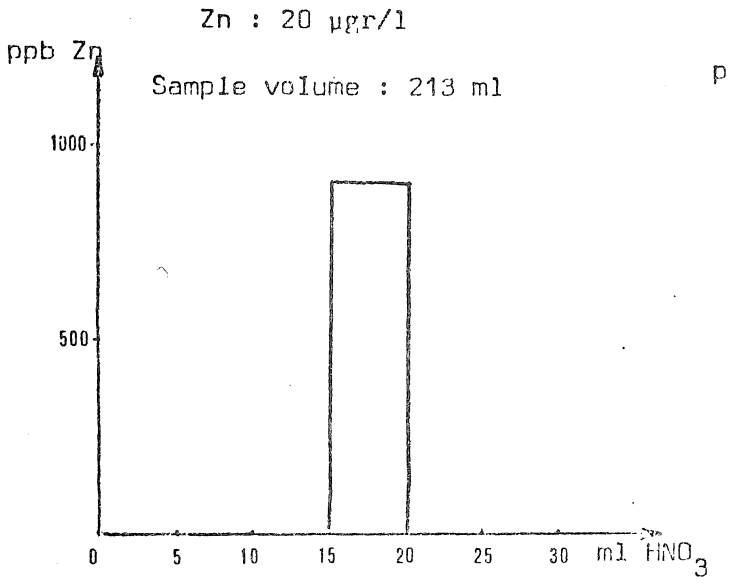


Fig. 1 : Zinc elution

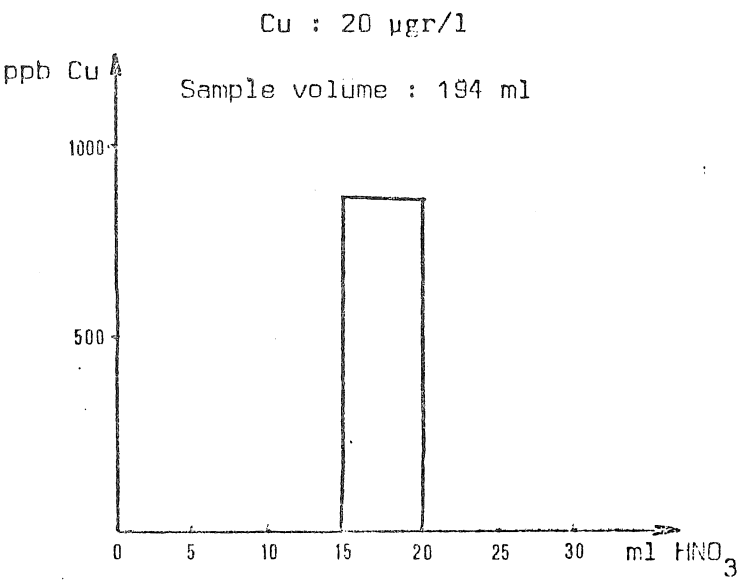


Fig. 2:: Copper elution

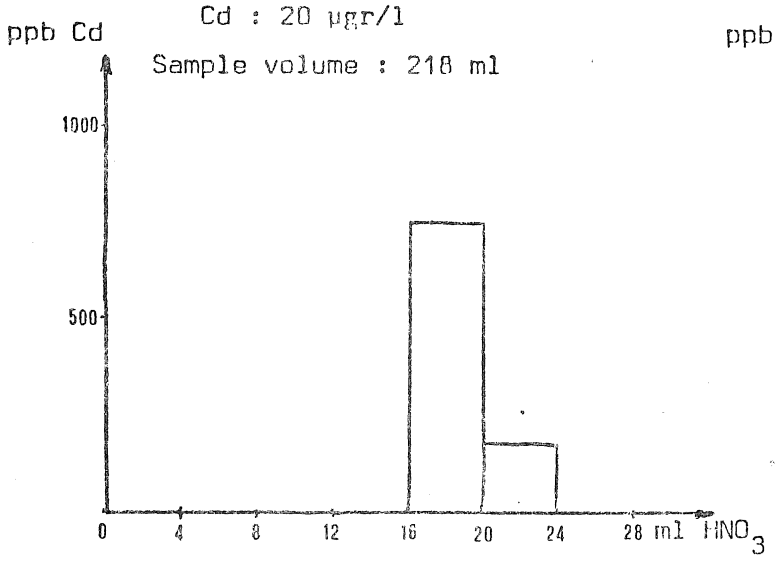


Fig. 3 : Cadmium elution

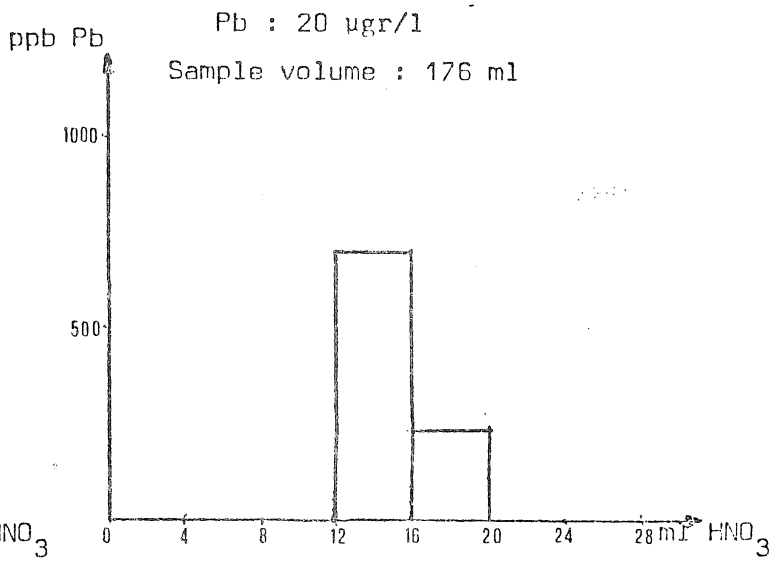


Fig. 4 : Lead elution

One thus obtains concentration factors that can reach 40 which allows, for coastal seawater, a flame analysis to be performed. For off-shore water, where lead and cadmium concentrations are very low, a greater sample volume will be necessary to avoid the use of the graphite furnace.

Reproductibility.

Five identical samples delivered by the Fisheries Laboratory of Lowestoft and filtered on 0.22 µm Millipore filter were analysed with and without increments of copper, zinc and cadmium.

The metals concentrations computed from the results of these two sets of analyses as well as the relative standard deviation obtained considering all these values are reported in the tables 1, 2 and 3.

TABLE 1 : ZINC CONCENTRATIONS.

Sample	Zn in µgr/l (without increment)	Zn in µgr/l (with 8 µgr/l increment)
A	9,9	8,9
B	8,8	9,5
C	9,4	9,5
D	9,4	9,3
E	8,5	11,8

S_R = 10 %

TABLE 2 : COPPER CONCENTRATIONS.

Sample	Cu in µgr/l (without increment)	Cu in µgr/l (with 2 µgr/l increment)
A		2,7
B	3,0	2,5
C	2,3	2,6
D	2,3	2,3
E	2,6	2,2

S_R = 11 %

TABLE 3 : CADMIUM CONCENTRATIONS.

Sample	Cd in µgr/l (without increment)	Cd in µgr/l (with 0,2 µgr/l increment)
A	0,10	0,095
B	0,09	0,09
C	0,07	0,105
D	0,11	0,09
E	0,11	0,11

S_R = 13 %

Results of the Intercalibration samples.

We have determined zinc, copper, cadmium and lead in samples we received from the Fisheries Laboratory of Lowestoft and from the Netherlands Institute for Sea Research of Texel which, with the Laboratory of Prof. Duyckaerts (University of Liege) and ourselves, are participating to an Intercalibration program concerning the heavy metals methods of analysis in the Northsea.

Seawater received from Lowestoft in January and March was sampled as followed : 20 x 1 L seawater were pumped in surface and filtered through 0.22 µm Millipore filter. These 20 liters were then mixed and divided into 20 samples which were distributed between Belgium, the Netherlands and the two laboratories of Lowestoft (Hydrography and Radiobiology).

The samples coming from Texel were also delivered filtered on 0.22 µm. The results we obtained are reported in the tables 1, 2, 3 and 4.

We have compared our values with those obtained in the two english laboratories which are using a concentration method by complexation and extraction with APDC-MIBK followed with atomic absorption measuring.(the difference between the ones made by the Radiobiology Laboratory and the Hydrography Laboratory lies in the fact that the APDC complex is extracted by means of chloroform).

The results obtained by these two methods of analysis, extraction and concentration on a resin, may indeed be compared because they both measure the "soluble" heavy metals present under the ionic or weak complexes form in seawater, without any pretreatment of the sample such as : acidification, photo-oxidation etc...

We were able to check an excellent correlation for the zinc concentrations (discrepancies are in the range of the standard deviation of the methods) and a rather good correlation for cadmium bearing in mind the very low measured contents.

For copper however our values are systematically higher (they average a factor 2) than the english ones. This discrepancy between the two methods has been quoted by Muzzarelli (3) who has found that, for samples of which the organic matter has not been destroyed by oxidation, synthetic (Chelex 100) or natural (Chitosan) resins extract more efficiently copper from seawater than the soluble complexing agents. We could not compare the lead values, this parameter not being determined by the Lowestoft laboratories.

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(3) R.A. MUZZARELLI, R. ROCCHETTI : Anal. Chim. Acta 69, 35 (1974).

INTERCALIBRATION SAMPLES FROM LOWESTOFT - SEPTEMBER 1973.

- Samples were filtrated on board through Millipore 0,22 µm.

Method : The samples were concentrated on an ion exchange column Chelex 100. Metals in the eluate were determined by atomic absorption spectroscopy.

Identification	Zn (µgr/ℓ)	Cu (µgr/ℓ)	Cd (µgr/ℓ)	Pb (µgr/ℓ)
H5 52°37'N 03°12'E (surface) CLIONE 13/73 - 11/9/73	5,5	1,9	0,17	0,89
J1 51°29'N 00°58'E (surface) CLIONE 13/73 - 12/9/73	5,7	3,3	0,87	0,57
K6 51°22'N 03°01'E (surface) CLIONE 13/73 - 13/9/73	3,5	3,0	0,73	0,67
L2 51°01'N 01°30'E (surface) CLIONE 13/73 - 14/9/73	4,6	1,6	0,40	0,65
J10 52°03'N 04°04'E (surface) CLIONE 13/73 - 13/9/73	6,9	2,8	0,69	0,57

TABLE 1

INTERCALIBRATION SAMPLES FROM LOWESTOFT - JANUARY 1974.

- Samples were filtrated on board through Millipore 0,22 µm.

Method : The samples were concentrated on an ion exchange column Chelex 100. Metals in the eluate were determined by atomic absorption spectroscopy.

Identification		Zn (µgr/ℓ)	Cu (µgr/ℓ)	Cd (µgr/ℓ)
Sample 6 51°50'N 02°55'E	(A)	3,0	1,8	0,09
CORELLA 12/1/74 (surface)	(E)	2,5	1,7	0,11
	(I)	2,9	1,7	0,11
	(M)	2,9	1,7	0,08
	(Q)	2,9	2,1	0,09
Sample 10 52°03'N 04°04'E	(A)	9,4	2,4	0,46
CORELLA 13/1/74 (surface)	(E)	8,8	3,0	0,48
	(I)	9,5	2,5	0,34
	(M)	9,4	2,3	0,35
	(Q)	10,1	2,7	0,48

TABLE 2

INTERCALIBRATION SAMPLES FROM LOWESTOFT - MARCH 1974.

- Samples were filtrated on board through Millipore 0,22 µm.

Method : The samples were concentrated on an ion exchange column Chelex 100. Metals in the eluate were determined by atomic absorption spectroscopy.

Identification		Zn (µgr/ℓ)	Cu (µgr/ℓ)	Cd (µgr/ℓ)	Pb (µgr/ℓ)
Station 5 51°29'N 00°46'E	(4)	1,3	1,2	0,23	0,70
	(8)	1,8	2,3	0,22	0,83
	(12)	1,4	1,8	0,20	0,59
	(16)	2,0	1,4	0,22	0,54
	(20)	1,8	1,4	0,22	0,50
Station 24 51°29'N 00°46'E	(4)	19,6	4,6	0,40	0,74
	(8)	20,1	4,3	0,33	0,91
	(12)	21,1	4,2	0,31	0,82
	(16)	20,7	4,2	0,33	0,79
	(20)	20,1	4,3	0,29	0,80

TABLE 3

- INTERCALIBRATION SAMPLES FROM TEXEL - JANUARY 1974.

- Samples were filtrated through Millipore 0,22 µm.

Method : The samples were concentrated on an ion exchange column Chelex 100. Metals in the eluate were determined by atomic absorption spectroscopy.

Identification	Zn (µgr/ℓ)	Cu (µgr/ℓ)	Cd (µgr/ℓ)	Pb (µgr/ℓ)
E 11/1/74	21,5	5,4	0,69	1,2
G 11/1/74	22,1	5,5	0,59	1,7
I 11/1/74	20,5	8,7	0,76	1,6
L 11/1/74	21,5	6,9	0,76	1,6
N 11/1/74	28,3	10,7	0,79	1,2

TABLE 4